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(54) **Cleansing compositions.**

(57) This invention relates to a water dispersible formulation which contains at least one ether alcohol, water and a hydrocarbon present in a single phase in a percent weight ratio range of ether alcohol (90-50) : water (2-36) : hydrocarbon (25-0.9), wherein the ether alcohol is of the formula

$$R^1O(RO)_nH \quad (I)$$

in which R is a C₁-C₄ alkylene group, n is at least 1, and R¹ is a C₁-C₄ alkyl or an aryl group.

The formulation is suitable for cleansing drill cuttings, rock cuttings, electronic components, army tanks, ships tanks and the like, and for removal of oils, waxes, greases and rosin precipitates from soiled surfaces.

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CLEANSING COMPOSITIONS

The present invention relates to a surface cleansing composition for removing oil adherent to surfaces e.g. rock cuttings produced during drilling operations for oil.

Rock cuttings are produced during normal drilling operations. The drilling fluids used in these operations normally carry these cuttings away from the drill bit up the annulus, between the drill pipe and the bore hole to the mud line and then to the drilling platform. If rock cuttings are not removed, periodically at least, they will build up in the drilling mud closed loop to the detriment of the drilling process as a whole. Thus, it is conventional to install a solids control system as part of this loop. The larger cuttings are usually removed by screen shakers and the sand and silt are removed by using hydrocyclones. When the fine colloidal solids build up in the mud they are generally removed by centrifugation in association with either an aqueous surfactant wash or dilution with base oil. When treating cuttings which predominantly comprise clay, it is currently the practice to use the base oil dilution/centrifugation technique, otherwise the cuttings would disintegrate in an aqueous wash solution giving rise to a stable dispersion of submicron particles, rendering the wash solution unsuitable for re-use.

The main requirement of any process for cleansing surfaces such as those of, e.g. rock cuttings is that it significantly reduces the amount of oil associated with the surface, e.g. cuttings being discharged into the environment e.g. sea, along with the effluents from the process. Currently legislation is being considered in the UK to reduce the oil content of such discharges to below 150g/kg of dry cuttings in the residue. This limit may be further reduced to a maximum of 100g/kg of dry cuttings in order to minimise pollution risks.

It has now been found that by using a specific formulation for cleansing oily surfaces, the oil contaminant on the surface can be reduced significantly.

Accordingly, the present invention is a water dispersible formulation suitable for use as a cleansing agent, said formulation comprising at least one ether alcohol, water and a hydrocarbon in a single phase in a percent weight ratio range of ether alcohol (90-50) : water (2-36) : hydrocarbon (25-0.9) and wherein the ether alcohol is of the formula



in which R is a C₁-C₄ alkylene group, n is at least 1, and R' is a C₁-C₄ alkyl or an aryl group.

The single phase formulation referred to above can be prepared by mixing at ambient temperature and pressure, water, kerosine and the ether alcohol in a percent weight ratio range of 3-60 : 0.9-60 : 10-90 respectively. In those cases where such a mixture separates into three phases, the middle phase of the three phases is the desired water dispersible formulation usable as a cleansing agent.

The water component of the formulation may be fresh water but in some cases it may be necessary to use saline water in order to aid middle phase formation. By 'saline water' as used herein is meant that the water contains one or more ionisable salts. Examples of such salts include the halides and sulphates of sodium, potassium, calcium, magnesium, ammonium and tetra alkyl ammonium ions. A typical example of saline water is sea water.

The water component of the formulation may thus contain from 0-5% w/w of the ionisable salts, preferably from 0.2-5% w/w of the salts. It is preferable to use saline water with ethoxypropoxy propanol or phenoxypropanol whereas fresh water is preferable when using 2-butoxyethanol or a mixture thereof with ethoxy propanol or ethoxypropoxy propanol. If phenoxypropoxypropanol is used, especially if the latter contains small amounts of phenoxy propanol, either saline water or fresh water can be used.

When using the formulation of the present invention, some of the substrates cleaned are prone to fines generation, eg. in the case of drill cuttings. In such cases it is preferable to add to the solvent a fines suppressant such as amino compounds which may be organic or inorganic. For instance this effect may be achieved by the ammonium salts referred to above, e.g. ammonium chloride or by compounds such as polyalkylene imines eg. polyethylene imine, tetraalkyl ammonium halides, eg. tetra-methyl-,ethyl-,propyl-, butyl or -pentyl ammonium chloride, and tris(hydroxymethyl) methylamine. The term hydrocarbon as used herein is meant to include any hydrocarbon fraction or mixtures thereof boiling in the range of 100-320 °C and containing predominantly paraffinic hydrocarbons. Examples of such hydrocarbons include kerosine, BP83HF (ex.BP), decane and mixtures thereof.

In the ether alcohol of the general formula (I), R is preferably a C₂-C₄ alkylene group and n preferably has a value from 1-4. Thus the ether alcohol may be 2-butoxyethanol, ethoxyethoxy-propanol, ethoxypropoxy-propanol, propoxyethoxy-propanol, propoxypropoxy-propanol, butoxyethoxyethanol butoxy butoxyethanol, phenoxy propanol and phenoxypropoxy propanol and mixtures thereof. One or more of these ethers can be used in combination with ethoxy propanol. Ethoxypropoxy propanol is however preferred. It will be understood that the references to 'ether alcohols' containing 3 or more carbon atoms in the alkyl

chain will include mixtures of one or more isomers. For instance the propoxyl units in an ether alcohol may include secondary propoxyl units.

The formulation described above can be used to cleanse surfaces contaminated by oil. The expression "oil" in this context is meant to include mineral oils, vegetable oils, synthetic hydrocarbon based lubricants/oils and greases.

These formulations can be used either as such or in conjunction with additives such as adhesion promoters, corrosion inhibitors, biocides, demulsifiers and the like.

The contaminated surface can be cleaned by contact with the cleansing formulation e.g. by immersion of the contaminated surface into the formulation, or by wiping the contaminated surface with the formulation, or by spraying the latter on the contaminated surface. For instance, the cleansing procedure used in general terms for deoiling rock cuttings associated with drilling for crude oil is as follows:

The single phase, water dispersible formulation comprising the three components is brought into contact with the surface, e.g. rock cuttings, contaminated with oil. Thereafter, the liquid phase is separated from the deoiled surface by e.g. pressure filtration or centrifugation.

The liquid filtrate then separates into an oily phase and a formulation phase comprising the ether alcohol, water and kerosine. This solvent phase can be reused for cleansing further contaminated surfaces.

The residual deoiled surface, e.g. rock cuttings can subsequently be washed off with any conventional solvents.

The formulations of the present invention have further advantages in that they:

(a) displace but do not emulsify the oil removed from the contaminated surface to any substantial extent,

(b) enable the separated oil to be easily skimmed or decanted off from the liquid phase and the formulation to be reused to treat a fresh sample of contaminated surface,

(c) enable any residual formulation on the deoiled surface to be washed off by water in which the formulation, unlike the oil contaminant, is dispersible and

(d) enable a significantly high proportion of the oil to be removed from the contaminated substrate when compared with conventional cleansing agents.

Whilst the formulations disclosed herein and their use is directed primarily towards removal of oil from drill cuttings, these formulations can be used equally efficiently to cleanse electronic components, army tanks, ships tanks, pumps and the like to remove oils, waxes, greases, rosin precipitates and the like.

Moreover, the formulations can also be used to displace water and to remove particles from surfaces. Adsorbed organic molecules may also be removed.

The present invention is further illustrated with reference to the following Examples.

Examples

1. Materials

A 5 litre sample of oily drilling mud cuttings was sampled from a well in the North Sea, UK.

The cleansing formulation used in this case was made by simply mixing the specific chemicals as shown in Table 1 at room temperature, hand shaking and then allowing the mixture to separate into three phases. Cyclohexane was used in the mixture to aid phase separation in the mixture.

The middle phase (the cleansing formulation) was extracted and used for the cleaning tests. This middle phase contained ethoxypropoxy propanol (EDP, ex BP Chemicals), water, cyclohexane and kerosine in the ratios shown in Table 1.

Table 1

Cleansing Formulation			
Component in mixture	Wt% of Components in the three phases		
	Upper	Middle	Lower
Sea Water	1.4	17.4	60.5
Cyclohexane	17.4	4.0	1.5
Kerosine	41.5	7.9	ND
Ethoxypropoxypropanol*	39.7	70.7	38.0

*The purity of this material was ca 87.0%

2. Experimental Method

A sample of drill cuttings contaminated with drilling mud (1-2g) referred to above was dispersed in 10 mls of the cleansing formulation, then pressure filtered at 20 psi in a Millipore stainless steel filter holder with a Whatman No. 5 filter. The mud cuttings were subsequently washed with two 30 ml aliquots of synthetically simulated sea water and similarly pressure filtered. The oil remaining on the cuttings after this cleansing treatment was then determined by extracting with two 50 ml aliquots of carbon tetrachloride and the level of oil measured by infra-red absorbance on a calibrated Miran IIA spectrophotometer. The weight of dry, extracted/deoiled residue was noted and residual oil quoted as g oil/kg dry residue.

The performance of the cleansing formulation of the present invention was compared with that of the conventional cleansing processes. Further samples of oily mud cuttings from the same source, as tested previously, were again dispersed in (i) aqueous surfactant solution (5%w/w aqueous solution of Byprox (Registered Trade Mark)), a dodecyl benzene sulphonate surfactant marketed by The British Petroleum Company p.l.c. and (ii) kerosine, then filtered, washed and solvent extracted in the same manner as previously.

3. Potential Re-cycle of the used Cleansing Formulation

An aliquot of the formulation which had been recovered from a previous drilling mud cuttings clean-up experiment was re-used with a fresh sample of oily mud and its deoiling capability measured as previously.

The results are tabulated in Table 2 below.

Table 2

Drilling Mud Cuttings - Deoiling Experimental Results		
Experiment No	Cleaning Solution	gm oil/kg Dry Residue
1*	None	187
2*	None	176
3	Cleansing formulation/sea water wash	61
4	"	23
5	"	24
6	Cleansing formulation/reused from Exp. 5	80
7*	5% Byprox**/sea water wash	132
8*	Kerosine/sea water wash	126

*Comparative Test not according to the invention.

**Registered Trade Mark, dodecyl benzene sulphonate surfactant

A number of further formulations were prepared by varying the relative concentrations of the components in the initial mixture which resulted in a three phase composition. These are shown in Table 3 together with the concentration of each of the components in the middle phase so produced.

Laboratory tests showed that each of the middle phases generated gave rise to a formulation which also removed crude oil from a glass substrate.

Table 3

Middle Phase Cleansing Formulations										
Components	1		2		3		4		5	
	Bulk	Middle Phase	Bulk	Middle Phase	Bulk	Middle Phase	Bulk	Middle Phase	Bulk	Middle Phase
Deionised Water	60	35.3	40	25.8	30	27.1				
Kerosine	10	9.6	40	3.9	30	12.7				
2-butoxyethanol	30	54.9	20	70.2	40	60.2				
Sea Water	25	27.1	20	19	15	14.1	12.5	10.9	15	19
Kerosine	25	4.6	20	7.1	15	10	12.5	12.1	30	7.9
EDP	50	68.3	60	73.9	70	75.9	75	77	55	73.1
Sea Water	60	4.2	40	5.0	30	3.3	20	6.0		
Kerosine	10	10.7	40	16.4	30	13.4	20	10.7		
Ph P	30	85.1	20	78.5	40	83.2	60	83.3		
Sea Water	40	4.6	30	5.6	20	7.1	10	7.7		
Kerosine	40	14.7	30	12.1	20	4.2	10	6.7		
Ph P*		9.8		11.1		14.6		15.9		
Ph DP*	20	70.8	40	71.2	60	74.0	80	69.6		
Deionised Water	60	5.4	30	5.9	20	7.2				
Kerosine	10	9.7	30	11.1	20	7.7				
Ph P*		9.8		10.5		13.1				
Ph DP*	30	75.0	40	72.4	60	71.9				
EDP - Ethoxypropoxy-propanol										
Ph P - Phenoxypropanol										
Ph DP - Phenoxypropoxy-propanol										

* - this was a sample of Ph DP containing PhP as impurity

In addition to the above the following bulk compositions which form a middle phase falling within the scope of the present invention which can also be used as cleansing formulations.

In the following Tables all concentrations are %w/w: water when followed by (a) means 10%w/w NaCl solution, by (b) means 10%w/w NH₄Cl solution and (c) means deionised water. All experiments were carried out at room temperature.

The following abbreviations have been used in the results tabulated below:

BE	-	Butoxyethanol
BDGE	-	Butoxyethoxyethanol
EDP	-	Ethoxypropoxypropanol
EP	-	Ethoxypropanol
Base Oil	-	BP83HF base oil (ex British Petroleum Co Plc.)
KERO	-	Kerosine
OD KERO	-	Odourless Kerosine

TABLE 4

BULK COMPOSITIONS FOR SYSTEMS WHICH FORM THREE PHASES						
SYSTEM	SOLVENT(S)	CONC RANGE	OIL	CONC RANGE	WATER	CONC RANGE
1	EDP	40-60	OD KERO	10-50	a	10-50
2	EDP	40-60	KERO	10-30	b	10-50
3	1EDP:3EP	30-60	KERO	10-60	a	10-50
4	1EDP:3EP	40-60	BASE OIL	30-50	a	10
5	1EDP:3EP	40-60	OD KERO	10-50	a	10-30
6	1EDP:1EP	40	BASE OIL	30-50	a	10-30
7	1EDP:1EP	40-60	OD KERO	10-50	a	10-50
8	3EDP:1EP	40-60	OD KERO	10-50	a	10-50
9	BDGE	40-60	KERO	10-50	a	10-30
10	1BDGE:1EDP	20-60	KERO	10-60	a	10-60
11	1BDGE:1EDP	40-80	BASE OIL	10-50	a	10-50
12	1BDGE:1EDP	40-60	OD KERO	10-50	a	10-50
13*	3BE:1EDP	40	DECANE	10	c	50

*Carried out at 40° C.

TABLE 5

EXAMPLES OF MIDDLE PHASE COMPOSITIONS										
COMPOSITION % W/W										
COMPONENT	BULK	MIDDLE	BULK	MIDDLE	BULK	MIDDLE	BULK	MIDDLE	BULK	MIDDLE
BP83HF BASE OIL							30	5.2	50	2.4
KEROSINE	30	22.3	10	6.9	50	11.6				
EDP	15	20.6	15	20.2	10	18.7	15	23.9	10	22.4
EP	45	49.4	45	54.0	30	51.7	45	60.0	30	58.3
* SALINE WATER	10	7.7	30	18.9	10	18.0	10	10.9	10	16.9
COMPOSITION % W/W										
COMPONENT	BULK	MIDDLE	BULK	MIDDLE	BULK	MIDDLE	BULK	MIDDLE	BULK	MIDDLE
BP83HF BASE OIL	10	1.4	50	2.8					30	3.9
KEROSINE					30	25.2	10	5.7	-	-
EDP	30	40.7	20	43.0	3	4.5	3	4.4	60	87.9
EP	30	37.6	20	39.6	57	62.8	57	68.2	-	-
* SALINE WATER	30	20.2	10	14.6	10	7.5	30	21.7	10	8.1

* Saline Water in Bulk Composition = 10% w/v sodium chloride solution

TABLE 6
EXAMPLES OF MIDDLE PHASE COMPOSITIONS

COMPOSITION % W/W													
COMPONENT	BULK	MIDDLE	BULK	MIDDLE	BULK	MIDDLE	BULK	MIDDLE	BULK	MIDDLE	BULK	MIDDLE	MIDDLE
BP83HF BASE OIL	30	1.9	10	0.9	20	2.5	10	3.9	60	2.3	10	1.9	
KEROSINE	-	-	-	-	-	-	-	-	-	-	-	-	
EDP	40	84.3	30	79.9	60	86.9	80	88.7	30	85.0	60	86.0	
* SALINE WATER	30	13.7	60	19.1	20	10.5	10	7.4	10	12.6	30	12.0	

* Saline Water = 10% w/v sodium chloride solution

Laboratory Centrifuge Testing

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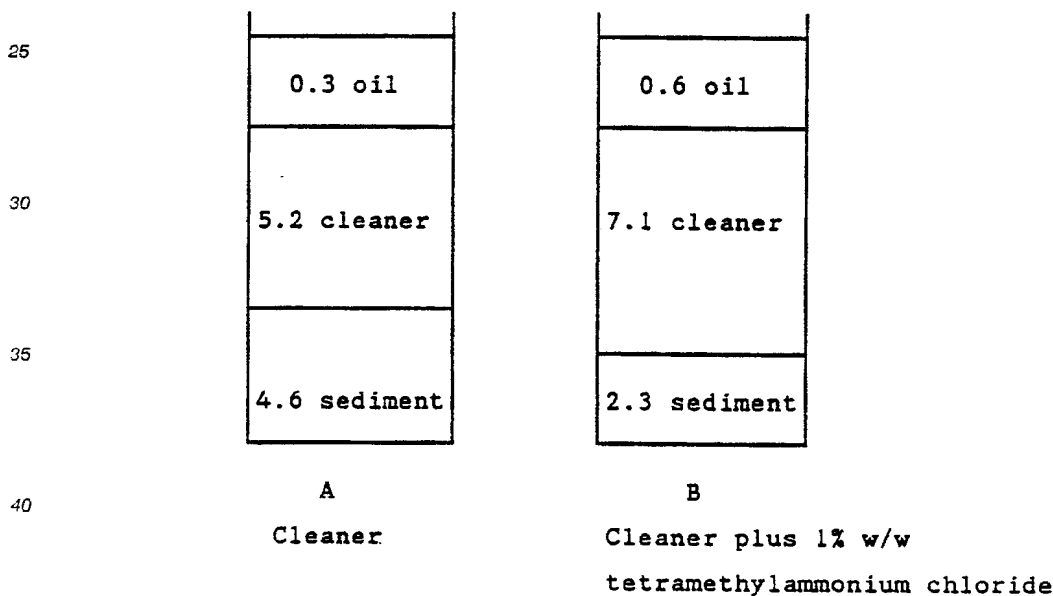
Experimental Technique

All the middle phase mixtures listed in Table 5 and 6 above have been tested in the laboratory by combining 30% w/w oily drill cuttings (typically <3mm in diameter and contaminated with 25-40% w/w oil based drilling mud) with 70% w/w middle phase cleaner.

The slurries were mixed for 30 seconds using a high shear mixer. Aliquots of the cuttings/cleaner slurry were then subjected to centrifugal force (MSE minor centrifuge, 2000 rpm for 5 minutes). The resulting samples exhibited the presence of three distinct phases ie rock sediment, cleaner and recovered oil. The volumes of each could be measured to give an indication of efficiency of oil removal and a measure of the rock sediment volume to give a level of effectiveness of added fines supressing agents. Specifically, 30g of oily drill cuttings from a land-based oil well were mixed as described with 70g cleaning solution having a composition, w/w, 19% sea water, 7.1% kerosine, 73.9% EDP and 10ml aliquots of the resulting slurry were separated using a centrifuge.

A further experiment where 1% w/w tetramethylammonium chloride was added to the cleaning solution was carried out in a similar way.

After centrifugation, the relative heights of sediment, cleaner and oil volumes were measured:



The results showed clearly that a good separation of rock cuttings, cleaner and oil was achieved under centrifugal force and that the addition of a fines supressing agent reduced the ultimate rock sediment volume.

Decanting Centrifuge Experiments

Experimental Technique

Samples of the middle phase cleaners were further assessed under decanting centrifuge conditions.

A 30% w/w slurry of oily cuttings in cleaner was fed to a laboratory scale decanting centrifuge (supplied by Thomas Broadbent and Sons Ltd, Huddersfield, UK) at 10-12 litres min⁻¹, and separated under a centrifugal force equivalent to 500 times gravity.

The treated solids produced were analysed for oil content by mud retort.
Two cleaners having the following compositions were tested:

5	i)	Ethoxypropoxypropanol	81.9% wt/wt
		Kerosine	7.4% wt/wt
		2% wt/wt sodium chloride solution	9.9% wt/wt
		Tetramethylammonium chloride	0.8% wt/wt
10	ii)	Ethoxypropoxypropanol	84.3% wt/wt
		BP83HF base oil	5% wt/wt
		2% wt/wt sodium chloride solution	9.9% wt/wt
		Tetramethylammonium chloride	0.8% wt/wt

15 The oily drill cuttings used in these experiments were from a land based well, had an average diameter of <3mm and were contaminated by 45% w/w oil from oil based drilling mud.

An additional cleaning experiment using low toxic base oil was carried out to simulate current cleaning procedure for decanting centrifuges on drill cuttings cleaning duties.

20 Retort analyses of the treated solids from each experiment showed oil-on-cuttings % w/w levels were as follows:-

	Residual oil % w/w
25 Cuttings as received	45
Base oil wash	12.5
Cleaner (i)	5.3
Cleaner (ii)	7.9

30 Further centrifugal processing of the recovered liquid(s) showed that the recovered oil split from the cleaner into two distinct phases allowing recovery of each.

Claims

35 1. A water dispersible formulation suitable for use as a cleansing agent, said formulation comprising at least one ether alcohol, water and a hydrocarbon in a single phase in a percent weight ratio range of ether alcohol (90-50) : water (2-36) : hydrocarbon (25-0.9) and wherein the ether alcohol is of the formula $R^1O(RO)_nH$ (I)

40 in which R is a C_1 - C_4 alkylene group, n is at least 1, and R^1 is a C_1 - C_4 alkyl or an aryl group.

2. A formulation according to claim 1 which is prepared by mixing in percent weight ratio ether alcohol : water : hydrocarbon in the respective ranges of 10-90 : 3-60 : 0.9-60 and, where such a mixture forms three phases, the formulation being the middle phase.

45 3. A formulation according to claim 1 or 2 wherein the ether alcohol is selected from ethoxy propanol, butoxyethoxyethanol 2-butoxyethanol, ethoxyethoxy-propanol, ethoxypropoxy-propanol, propoxyethoxy-propanol, propoxypropoxy-propanol, butoxy butoxyethanol, phenoxy propanol and phenoxypropoxy propanol and mixtures thereof.

4. A formulation according to any one of the preceding claims 1-3 wherein the water used contains one or more ionisable salts.

50 5. A formulation according to any one of the preceding claims wherein the water used is sea water.

6. A formulation according to claim 4 or 5 wherein the ether alcohol is ethoxypropoxypropanol or phenoxypropanol.

7. A formulation according to any one of the preceding claims 1-3 wherein the water used is fresh water and the ether alcohol is 2-butoxyethanol or a mixture thereof with ethoxypropanol or ethoxyethoxypropanol.

55 8. A formulation according to any one of the preceding claims wherein said formulations also contains a fines suppressant.

9. A formulation according to any one of the preceding claims wherein the fines suppressant is selected from ammonium halides, tetraalkyl ammonium halides, polyalkylene imines and tris(hydroxymethyl) methyl amine.

10. A formulation according to any one of the preceding claims wherein the hydrocarbon is kerosine,
5 BP83HF, decane or mixtures thereof.

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